



# ADVANCED CATALYSTS FOR DIRECT METHANOL FUEL CELLS

Jay Whitacre and S. R. Narayanan  
Jet Propulsion Laboratory  
Contract : DE-

DoE Hydrogen Fuel Cells and  
Infrastructure Technology  
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# Program Objectives

## *Overall Objective:*

- Develop catalysts for direct methanol fuel cells with substantially reduced amounts of noble metal loading for direct methanol fuel cells

## *Specific objectives:*

- Reduce noble metal loading below  $0.5 \text{ mg/cm}^2$
- Develop non-noble metal anode catalysts

# Budget

- Total FY04 funding: \$100K
- No sub-contracts

# Technical Barriers and Challenges

## Overall challenge for consumer electronics

- Target of \$ 5/Watt and a system power density of 30 W/kg by 2006
- Reduction in catalyst and stack materials cost and increase of performance

## Specific Technical Challenges and Barriers:

- Non-noble metals corrode in acidic media
- Catalyst discovery process is time intensive
- Wet chemical methods of preparation are inherently limited in creating new compositions
- Need methods which will be easy to implement for manufacturing
- The rationale for catalyst design is still largely empirical

# Non-Noble Metal Thin Film Catalyst layers

## Motivation

- Identifying alternates to precious metal catalysts
- Developing noble metal and non-noble metal combinations to reduce precious metal loading and enhance activity

## Approach

- Take advantage of sputter-depositon to identify a corrosion resistant non-noble metal system
  - non-equilibrium phases, unique nanophase structure, morphology and electronic properties.
- Ni/Zr system as proof-of-concept
- Characterization:
  - Corrosion studies in sulfuric acid, XRD, SEM
  - Fuel Cell studies with Ni-Zr/Pt-Ru catalyst layers

# Approach

## Overall Approach:

Develop catalysts with non-noble metal diluents that will be corrosion resistant and provide enhanced catalytic activity.

## Specific Approach

- Focus on Pt/Ru/Ni/Zr system that has been shown to be corrosion resistant and catalytically active.
- Deposit ultra thin (<10 nm) nanophase catalyst layers by sputterdeposition
- Develop combinatorial approach to rapidly deposit samples of various compositions
- Develop rapid parallel analyses techniques to determine activity
- Understand analytical results with theoretical constructs to extend field of fuel cell catalysis
- Evaluate selected materials in actual cells to determine performance

# Tasks and Schedule

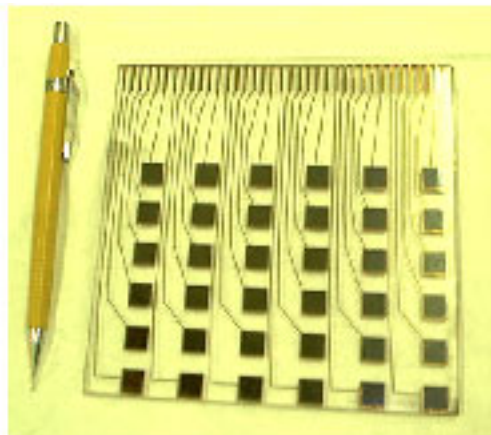
<u>Task</u>	<u>Completion date</u>
Screening of non-noble metal systems:	02/28/04
Preparation of combinatorial samples :	04/30/04
High throughput evaluation of properties :	06/30/04
Characterization in full cells	09/30/04

## Phase II ( proposed)

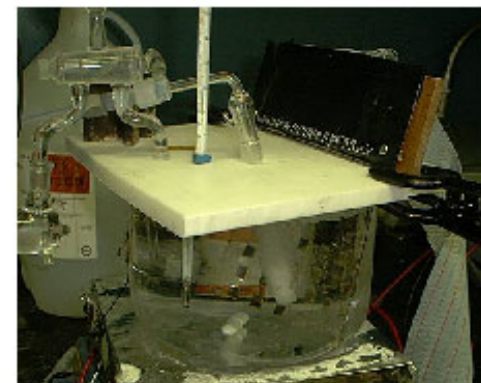
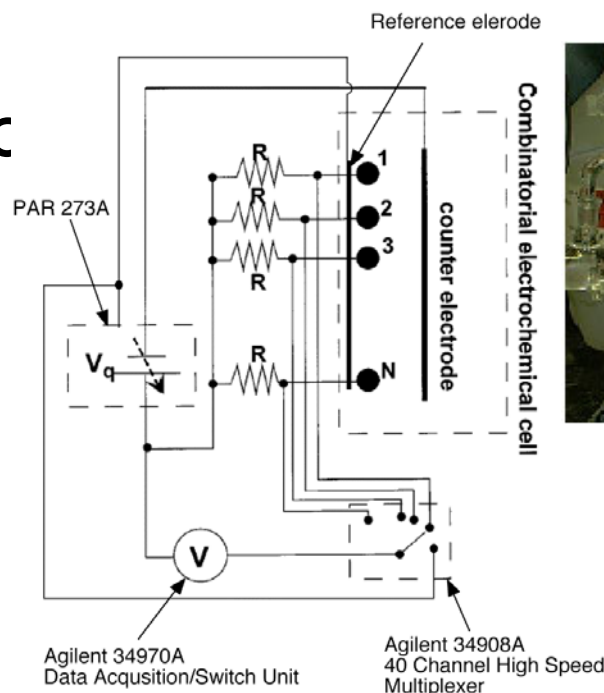
Demonstration of scaled up version of catalysts and membrane electrode assemblies and demonstration in stacks.

# Accomplishments

- Combinatorial sputter-deposition technique developed
- Combinatorial electrode sample evaluation technique developed and tested
- Pt/Ru/Ni/Zr catalysts samples have been tested



- 36-electrode array: Ti/Au patterned on 5x5" glass
- 100-150 Å Catalyst layers sputtered onto squares
- Physical mask used

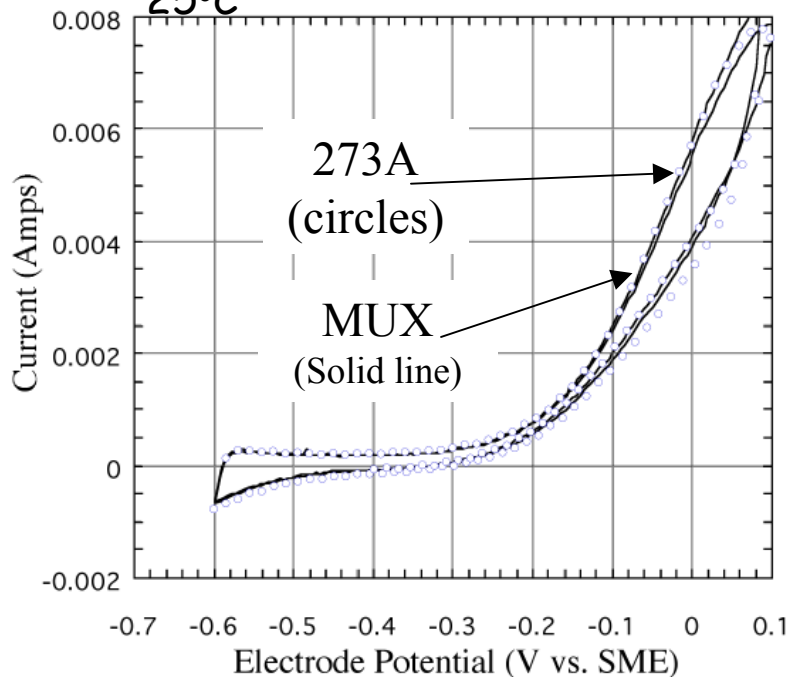


System in use 1 M H<sub>2</sub>SO<sub>4</sub>/1M Methanol solution. Gold spring-loaded pin contacts used for quick set-up



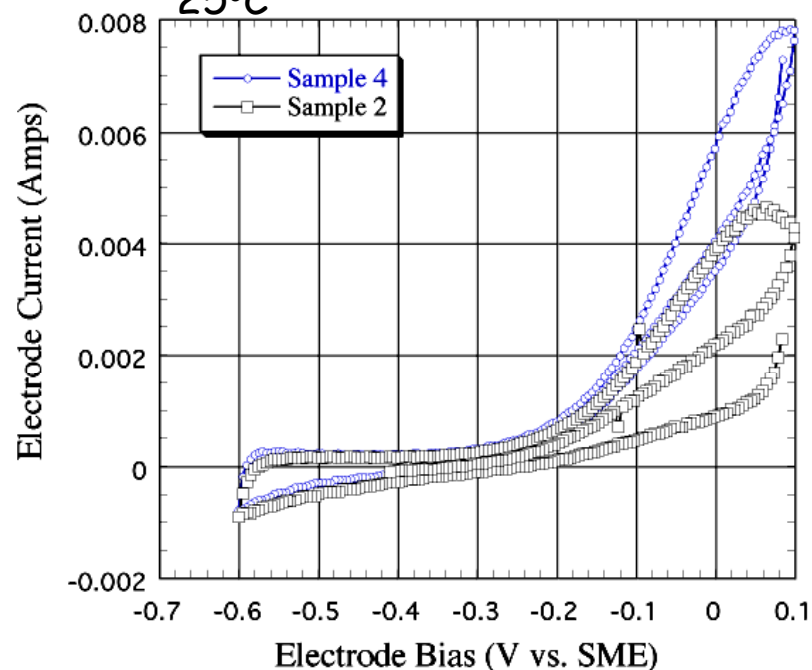
# Qualification of Combinatorial Test Station

Cyclic Voltammetry: 5mV/s in 1M methanol, 1M sulfuric acid at about 25°C



Good agreement between single potentiostat and multi-channel polarization scan

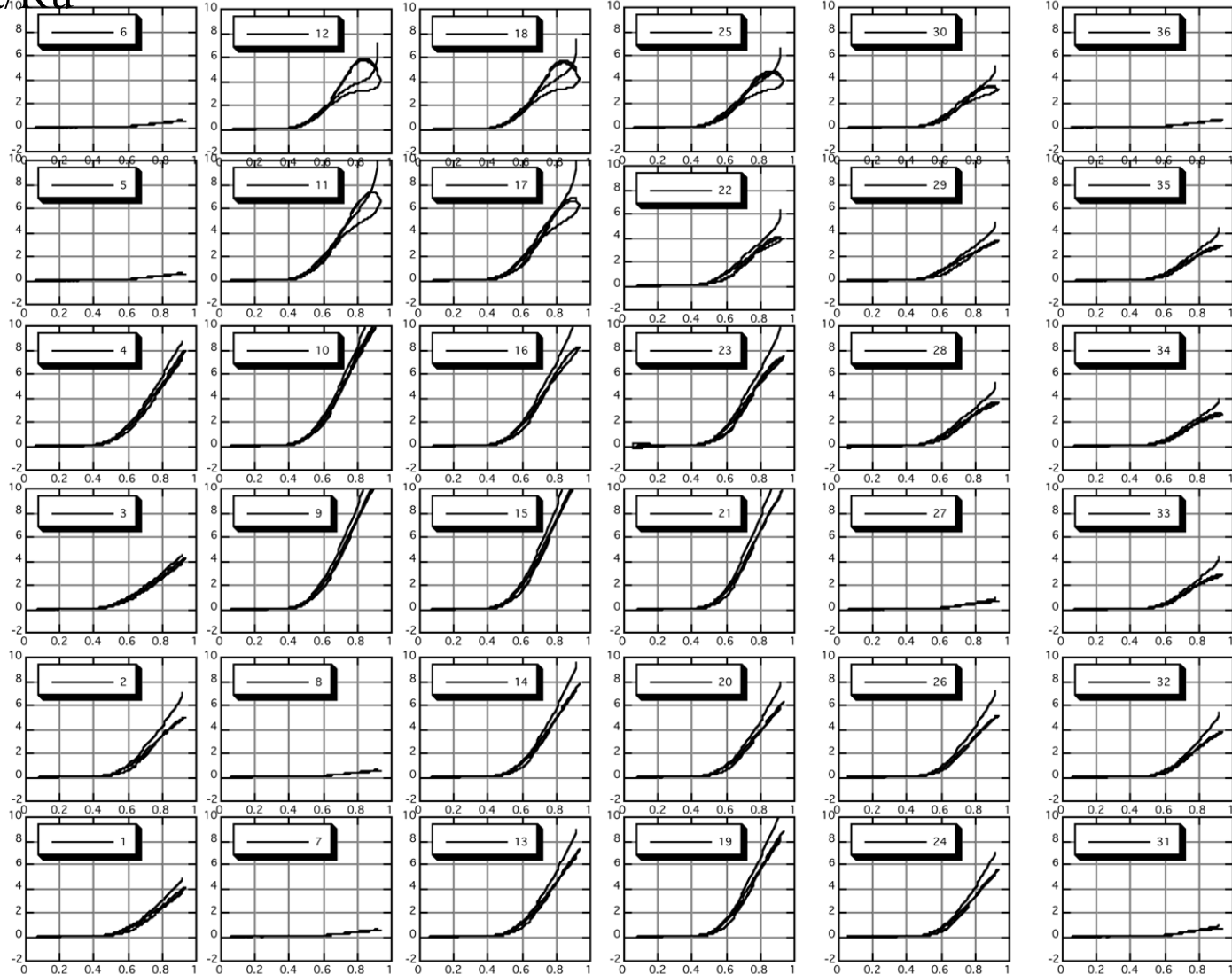
Cyclic Voltammetry: 5 mV/s in 1M methanol, 1M sulfuric acid at about 25°C



Different electrode performances well resolved in multichannel polarization scans

# Results of Parallel Polarization Scans

Pt/Ru



Pt

Ni/Zr

36 Cyclic voltammograms can be collected in parallel

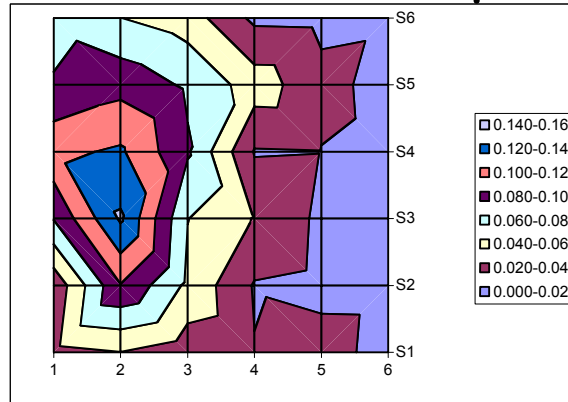
# Mapping the Performance of Various catalysts

Potentiostatic Data: 0.45 Vs NHE after 300 Seconds

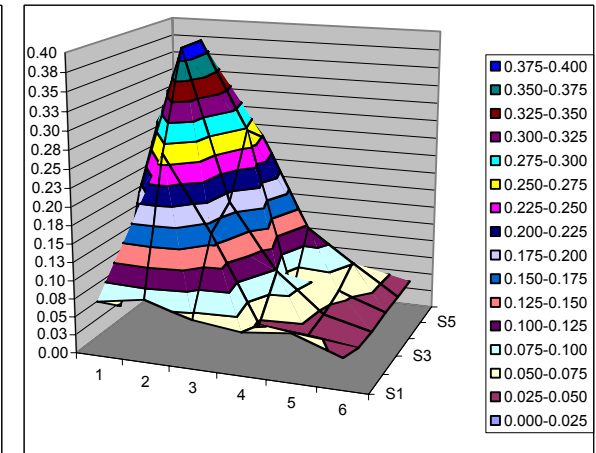
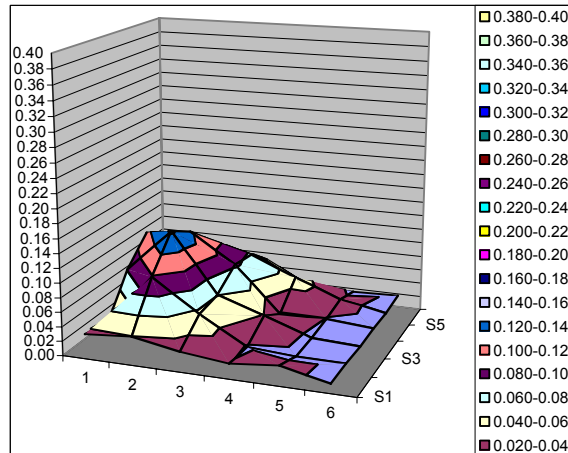
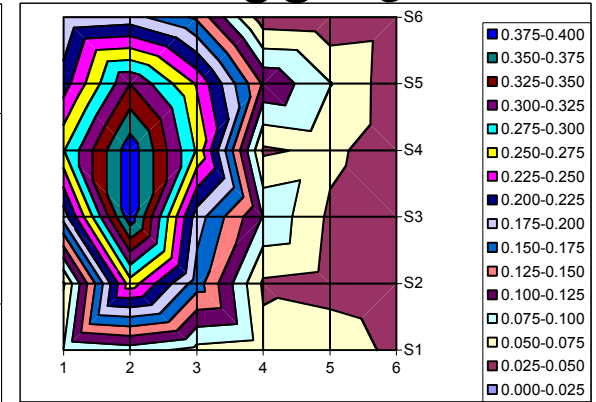
Cell Current (mA/cm<sup>2</sup>) as a function of composition

- Each grid intersection is a different test cell
- Each location is a different composition
- Plotting steady state potentiostatic current allows for "sweet spot" compositions to be identified
- Trends can be easily visualized
- Best cell in this case: #9, (Pt/Ru/Ni/Zr, ~70% Pt)

Room Temp

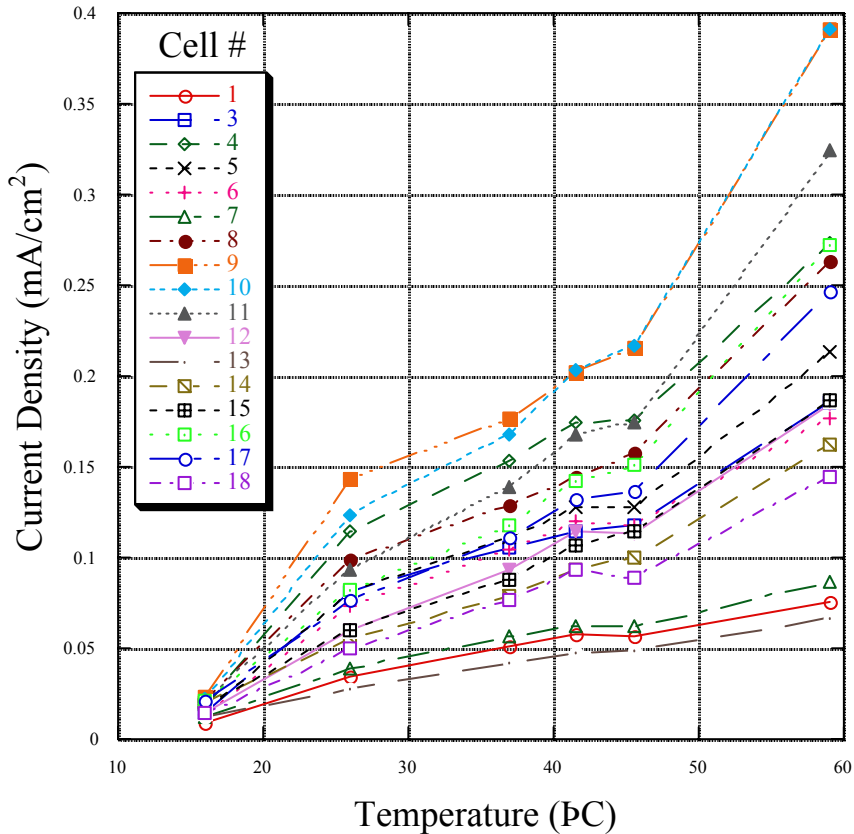


58 °C

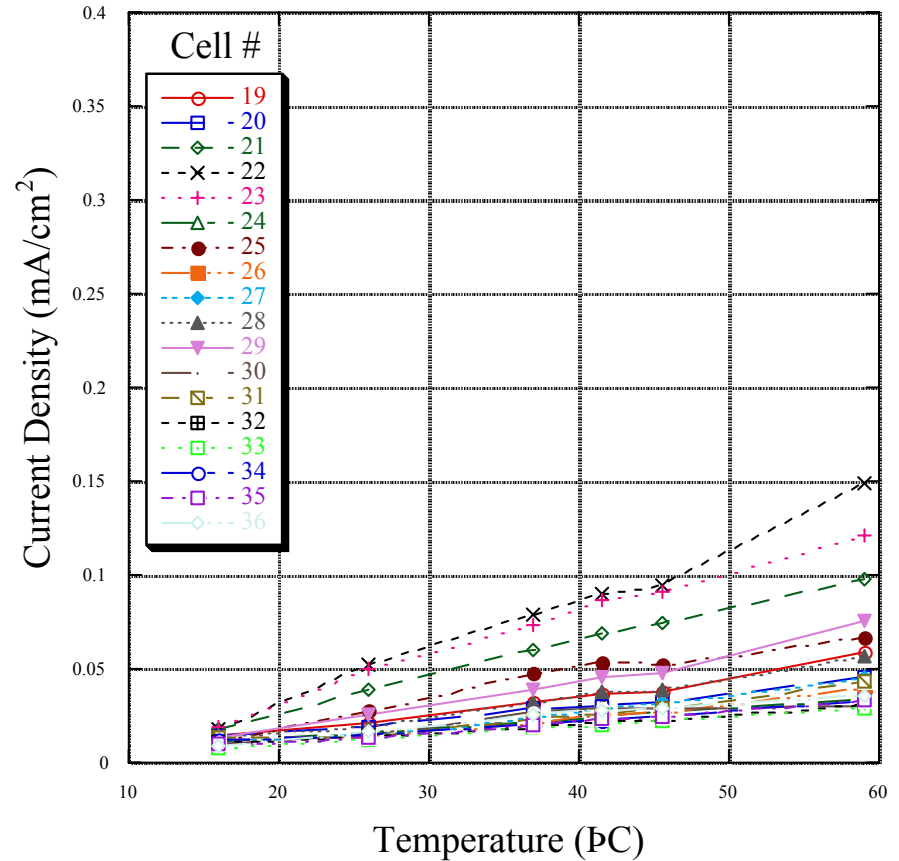


# Effect of Temperature on Catalytic Activity

Potentiostatic Data:  
0.45 vs. NHE after 300 seconds



Potentiostatic Data:  
0.45 vs. NHE after 300 seconds

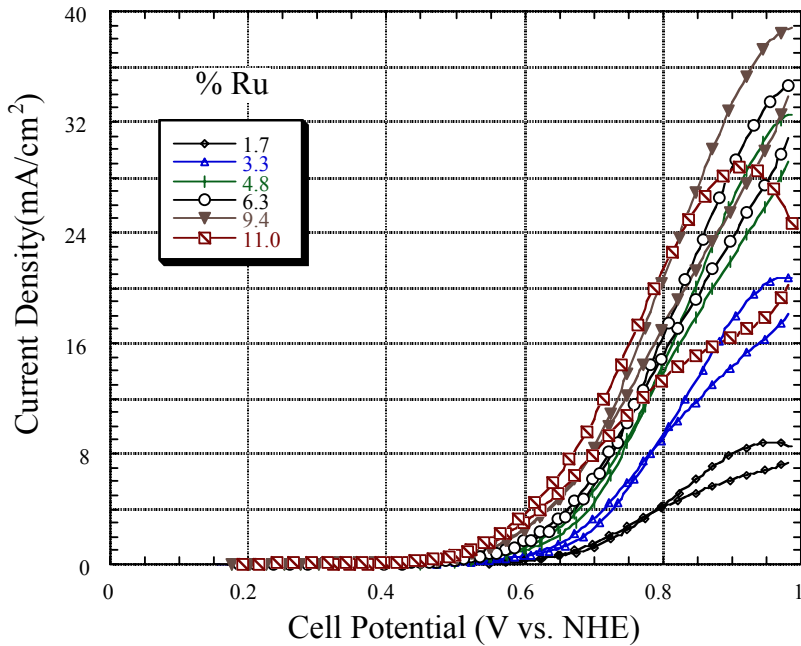


Effect of temperature varies with composition

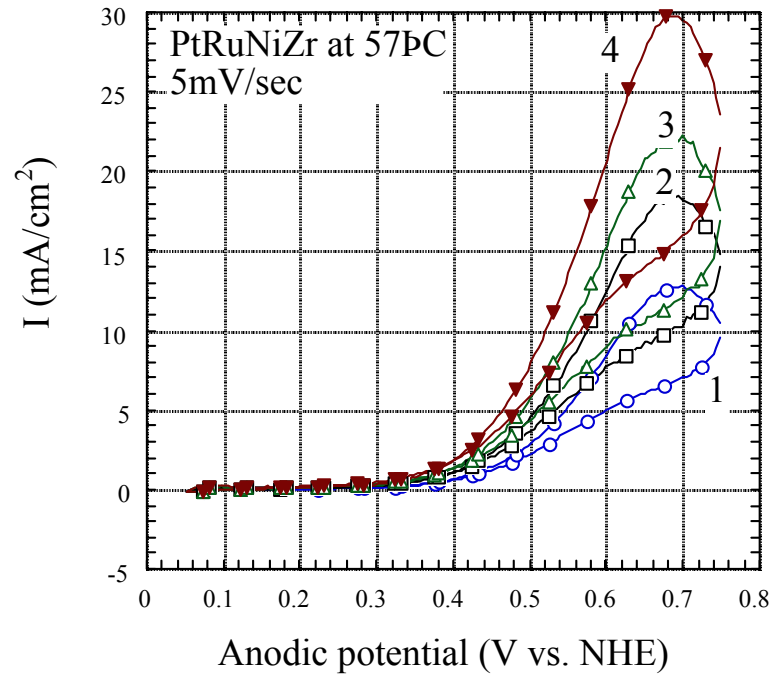
Activation energy and composition can be correlated to understand factors affecting catalysis.

# Comparison of Pt/Ru/Ni/Zr with Pt/Ru

Pt/Ru



Pt/Ru/Ni/Zr,



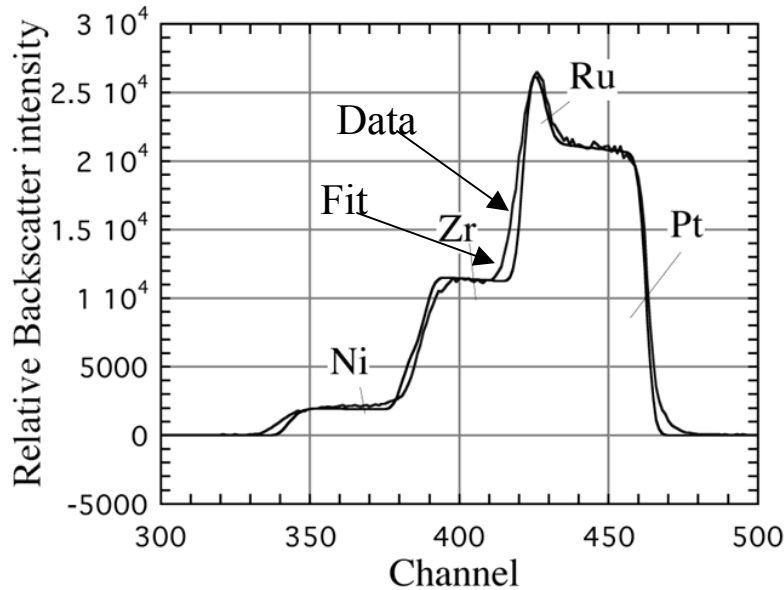
- Increase in performance observed using Pt/Ru/Ni/Zr over Pt/Ru
- Preliminary result - other combinations possibly more catalytic

# Compositional Analysis

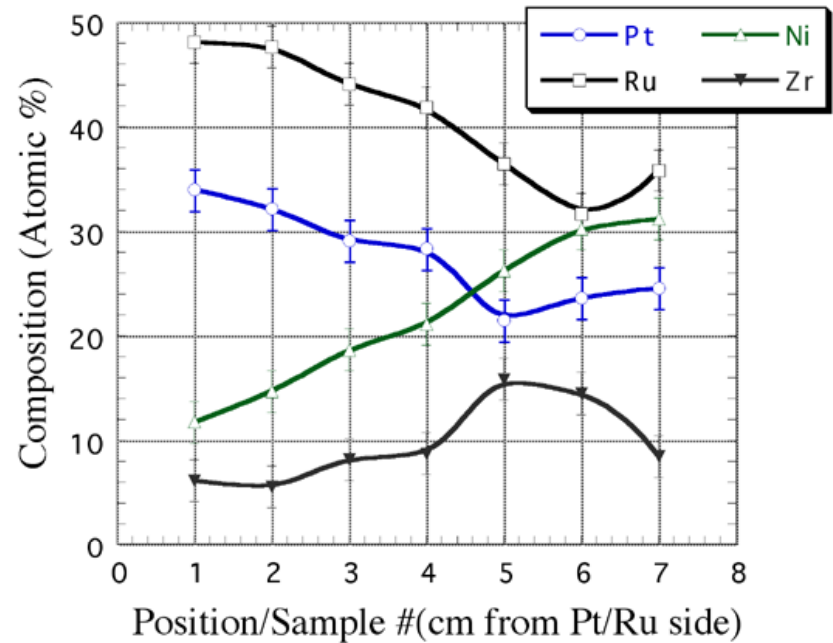
Rutherford Backscattering Spectroscopy  
Energy Dispersive X-ray Analysis



RBS Analysis



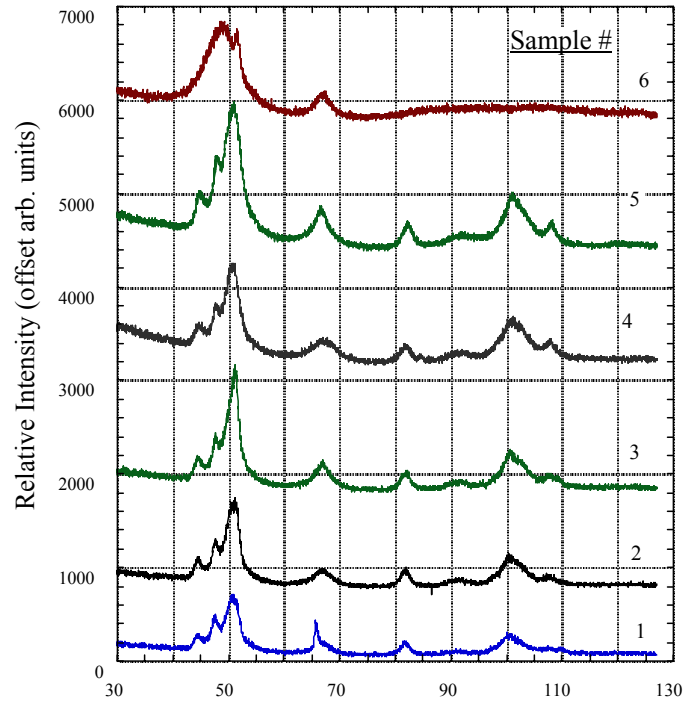
RBS Full Compositional Analysis



- Accurate fitting possible
- True quantitative compositional analysis

- Significant compositional variation across wafer
- Need to examine electrochemically

# JPL Crystalline Structure Of Pt/Ru/Ni/Zr Materials



- Thicker films ( $>100$  nm) studied using traditional x-ray diffraction
  - Solid state solution found from samples #1-5 (see previous slide for compositions)
- 10 nm thick films to be evaluated at SSRL

# Collaborations

All unfunded:

- SSRL for X-ray Scattering Data
- Univ. Southern California for XPS data



# Response to Reviewer's comments

- Insert here later

# Plans

## Remainder of FY04

- Complete characterization of Pt/Ru/Ni/Zr compositions
- Verify performance in full cells

## FY 05 (Proposed)

- Develop novel fundamental rationale for catalyst design based on wealth of combinatorial data in collaboration with Caltech.
- Extend investigation to new compositions involving cobalt
- Scale up and demonstrate in large MEAs and stacks for durability testing